

PHENOLS

Structure

16.1 Introduction	Reactions due to Phenolic Hydroxyl Group
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16.3 Physical Properties	Oxidation of Phenols
16.4 Preparation of Phenols	Condensation Reactions
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Acidity and Basicity of Alcohols and Phenols	Libermann's Nitroso Reaction
Reactions of Phenols	16.6 Summary
	16.7 Terminal Questions
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16.1 INTRODUCTION

In the previous Unit, we have discussed the chemistry of alcohols. In this Unit, we will discuss another class of compounds have hydroxyl group called phenols. The phenols are grouped as a separate class of compounds because their chemical properties are quite different from alcohols.

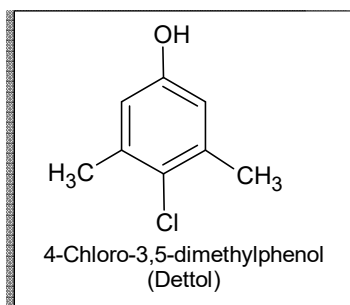
Phenols are aromatic compounds in which hydroxyl group(s) is attached to the benzene nucleus. Their general formula is $\text{Ar}-\text{OH}$, where Ar is phenyl, substituted phenyl, or some other aryl group. These compounds have several applications and are indispensable in our daily life. Phenolic functional groups are often encountered in a variety of household disinfectants, pharmaceuticals, agrochemicals and polymer materials. Phenol-formaldehyde resins, the polymers derived from phenols, for example, are the most widely used industrial polymers.

In this Unit, we will discuss general preparations and the chemical properties of phenols. Phenols are important both as substrates and as reagent. Phenols can be derivatised either at the hydroxyl group or the aromatic ring.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ classify phenols;

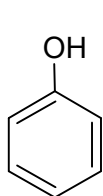


- ❖ explain physical properties of phenols;
- ❖ outline the preparation of phenols; and
- ❖ describe the reactions of phenols.

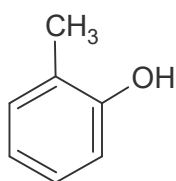
16.2 STRUCTURE AND REACTIVITY

Phenols are aromatic compounds in which hydroxyl groups are attached to the benzene ring; so they have the hydroxyl group on an aryl sp^2 hybridised carbon. Before going to detail of their structure and reactivity, let us recall some important aspects of their classification and nomenclature. Phenols are classified as mono-, di- or tri- hydric on the basis of the number of $-OH$ groups present in the ring. Some examples of phenols are given below.

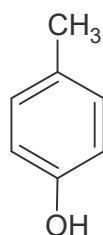
Monohydric Phenols



Benzenol
(phenol)



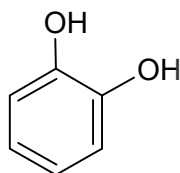
2-Methylbenzenol
(*o*-cresol)



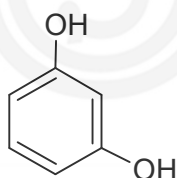
4-Methylbenzenol
(*p*-cresol)

Although benzenol is the systemic name of C_6H_5OH , the IUPAC rules permit 'phenol' to be instead.

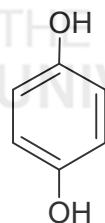
Dihydric Phenols



1,2-Benzenediol
(catechol)

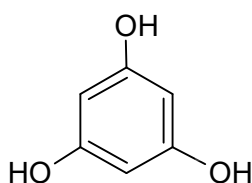


1,3-Benzenediol
(resorcinol)

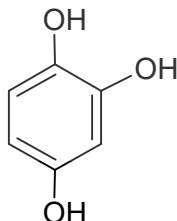


1,4-Benzenediol
(quinol or hydroquinone)

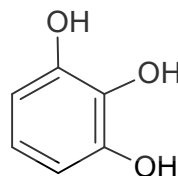
Trihydric Phenols



1,3,5-Benzenetriol
(phloroglucinol)



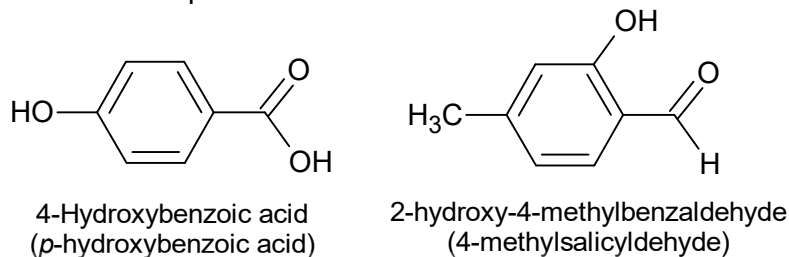
1,2,4-Benzenetriol
(hydroxyquinol)



1,2,3-Benzenetriol
(pyrogallol)

The common names of important phenols are still widely used; therefore, in this text we use both common names and IUPAC names. In the IUPAC system, substituted phenols are named as derivatives of benzenols. Numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in the direction that gives the lower number to next substituted carbon. Substituents are cited in alphabetical order. The prefixes ortho (*o*), meta (*m*) and para (*p*) are also

used to indicate the relative positions of substituents. The dihydroxy and trihydroxy derivatives of benzene are named as benzenediol and benzenetriol, respectively with the relative positions of hydroxyl groups in ring. If one of substituent is carboxyl or acyl group, then hydroxyl(s) group is treated as a substituent. For example:



You might expect phenols to be very similar to alcohols as they also have the hydroxyl group. But when we go in details of the structure of a phenol, we find the bonded aromatic ring interacts with the -OH group and in many aspects reactions of phenols are quite different from those of alcohols. Let us study in details of the structure of a phenol.

The carbon-oxygen bond lengths of phenol and alcohol are 136 and 142 pm, respectively.

The hydroxyl functional group (-OH) in a phenol is bonded to a sp^2 hybridised aromatic carbon atom. The oxygen atom of hydroxyl group, similar to an alcohol is sp^3 hybridised. The two sp^3 hybridised orbitals of oxygen form σ bonds to carbon atom of aromatic ring and hydrogen atom and the remaining two sp^3 hybridised orbitals each contain a lone pair of electrons. Similar to aryl halides, interaction between the delocalised electrons in the benzene ring and the lone pairs on the oxygen atom is also possible in phenols (see Fig. 16.1). This interaction causes partial double bond character in C-O bond. Thus, because of these two factors i.e. the increased s character of the sp^2 hybridised carbon and resonance delocalisation of electron pair of oxygen with aromatic ring, the C-O bond in phenol will be shorter and stronger than of an alcohol. This can be confirmed by measurement of bond lengths. The carbon-oxygen bond lengths of phenol and alcohol are 136 and 142 pm, respectively.

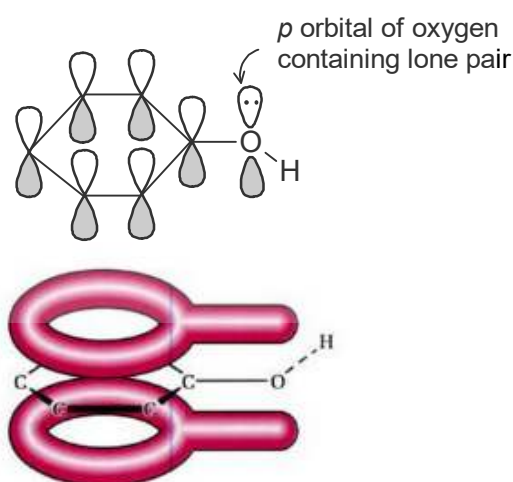
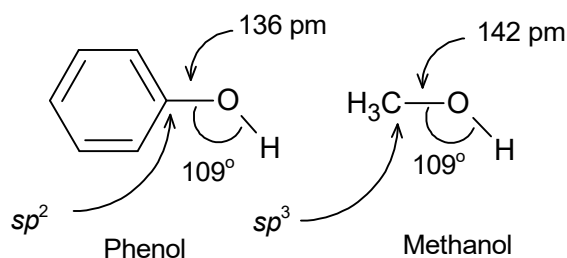


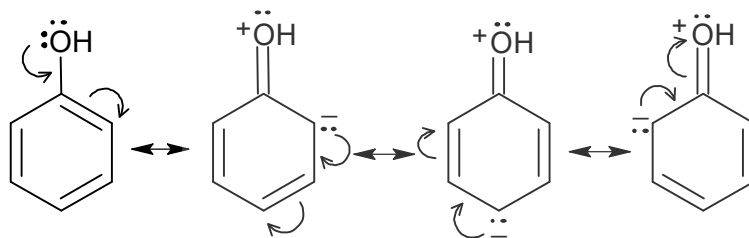
Fig. 16.1: Interaction of the lone pair of oxygen with the aromatic ring system

The geometry around oxygen atom of phenol is essentially the same as that in alcohols. The C-O-C angle has the tetrahedral angle of 109° . Further, both the C-O and the O-H bonds are polar in nature due to the high electronegativity of the oxygen atom. All these structural aspects of phenols

have an important effect on both the properties of the ring and of the -OH group.



The delocalisation of lone pair electrons of oxygen onto benzene ring can be shown by following resonating contributing structures:



The resonance effect shown by these contributing structures along with other structural features discussed above can explain many of the unique properties of phenols. Examples are as follows:

- Electrophilic aromatic substitution in phenols is much faster than benzene. This is because of the strong delocalisation effect of lone pair electrons of oxygen. In phenols, the hydroxyl group activates the ring, and therefore, it is ortho-para directing during electrophilic substitution reactions. The ortho-para directing nature of hydroxyl group can be understood by the resonating structures shown above for phenol, these structures clearly indicate that benzene ring is relatively electron rich at the positions ortho and para to hydroxyl group.
- Phenols generally do not undergo nucleophilic substitution reactions. The resonance effect also reduces the partial positive charge on the carbon bonded to the oxygen by spreading it over the whole delocalised benzene ring system and thus, making this carbon less susceptible to attack by nucleophile than the corresponding carbon in alcohols. Because of this factor and partial double bond between carbon and oxygen, phenols generally do not undergo nucleophilic substitution reactions (see Fig. 16.2).

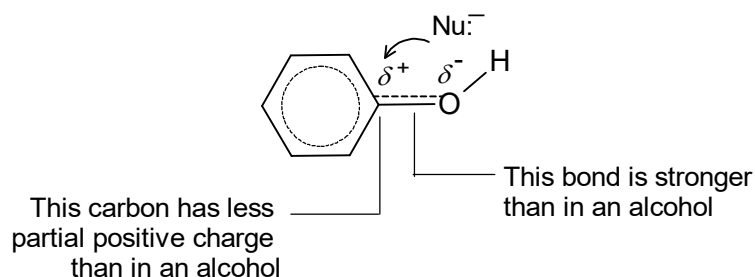


Fig. 16.2: Phenols are less susceptible to attack by nucleophiles than alcohols.

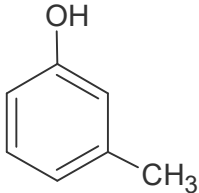
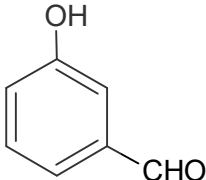
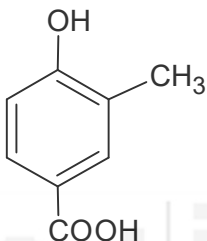
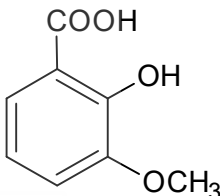
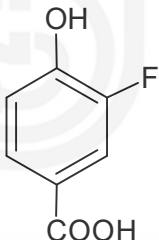
- Phenols are more acidic than alcohols. Benzene ring also contributes

towards bond polarisation of O–H bond and stabilisation of phenoxide ion formed after ionization of phenol. These factors result in more acidic hydroxyl proton and more basic hydroxyl oxygen in phenols in compared to alcohols.

We will further go in details of these properties in successive sections, but before that try following SAQs.

SAQ 1

Write IUPAC names of the following:

- i) 
- ii) 
- iii) 
- iv) 
- v) 

SAQ 2

Explain, why the C–O bond in phenols is shorter and stronger than the C–O bond in alcohols?

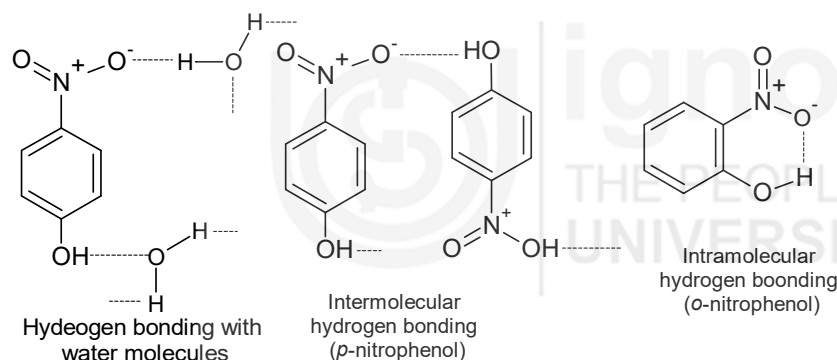
16.3 PHYSICAL PROPERTIES

Like alcohols, the physical properties of phenols are also strongly influenced by the hydroxyl group. Due to the polar nature of the O–H bond (both atoms have different values of electronegativity); phenols form hydrogen bonds with other phenol molecules and H-bonding systems like water. Thus, phenols also have high boiling points and moderate solubility in water compared to analogous aromatic hydrocarbons. On exposure to air and light they turn pink due to auto-oxidation. The physical properties of some phenols are summarised in Table 16.1.

Table 16.1: Physical properties of some phenols

Name	MP, K	BP, K	Solubility g/100 g H ₂ O
Phenol	314	455	9.3
Catechol	377	–	45.0
Resorcinol	383	–	123.0
Hydroquinone	446	–	8.0
<i>o</i> -Nitrophenol (volatile in steam)	318	–	0.2
<i>p</i> -Nitrophenol (nonvolatile in steam)	387	–	1.7

In Table 16.1, we notice that *ortho* and *para* isomers of nitrophenol differ considerably in their physical constants. How are we to account for these differences? Let us see how these isomers undergo hydrogen bonding:



From the above, we can expect that the *p*-isomer should have a higher melting point and solubility in water due to the **intermolecular hydrogen bonding** and its association with water molecules. On the other hand, *o*-nitrophenol has **intramolecular hydrogen bonding** or hydrogen bonding within a single molecule. It does not associate with other molecules or with water and, therefore, has lower melting point and lower solubility.

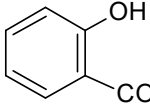
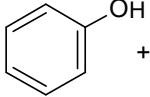
SAQ 3

The melting points of 2-fluorophenol and 4-fluorophenol are 289.1 K and 321.6 K, respectively. How will you account for these differences?

16.4 PREPARATION OF PHENOLS

Phenols can be prepared from arylsulphonic acid, phenolic acids, diazonium salts and from Grignard reagents. The general reactions of these methods of preparation are summarised in Table 16.2.

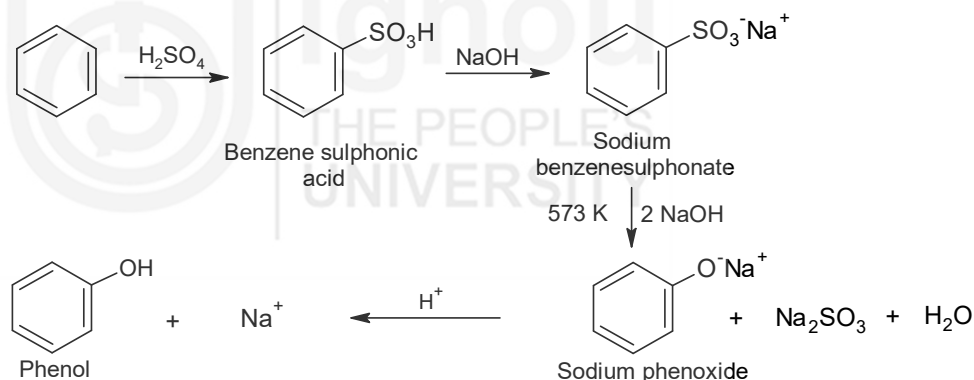
Table 16.2: Preparation of Phenols

Fusion of arylsulphonates with sodium hydroxide	
ArSO_3Na	$\xrightarrow[2. \text{H}^+]{1. 573 \text{ K/NaOH}}$ Ar-OH Phenol
Heating phenolic acid with soda-lime	
 $+ 2 \text{NaOH (CaO)}$	\longrightarrow  $+ \text{Na}_2\text{CO}_3$
Boiling diazonium salt with water	
ArN_2^+X^-	$+ \text{H}_2\text{O} \longrightarrow \text{Ar-OH} + \text{HX} + \text{N}_2$
Action of oxygen on Grignard reagent followed by hydrolysis	
$2\text{ArMgX} + \text{O}_2$	$\longrightarrow 2\text{ArOMgX} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} 2\text{ArOH}$

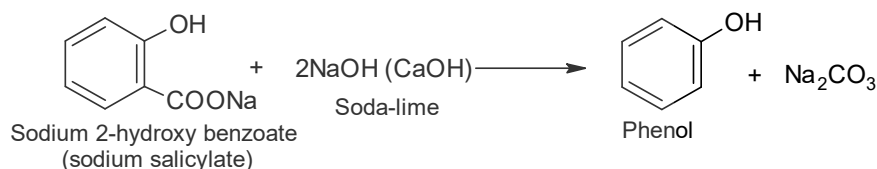
Let us study these reactions one by one.

i) Fusion of arylsulphonate with sodium hydroxide:

Phenol may be prepared by the fusion of sodium benzenesulphonate obtained through sulphonation of benzene (Unit 11), with sodium hydroxide. The sodium phenoxide produced in the reaction is converted into the free phenol by treatment with acid.

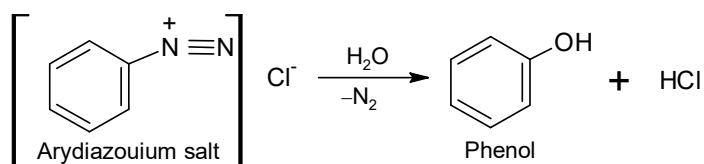


ii) Decarboxylation of phenolic acids with soda-lime:



iii) Boiling diazonium salt with water:

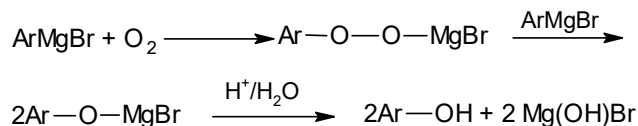
Aromatic amines react with nitrous acid to give diazonium salts which, unlike their aliphatic analogues, are stable at low temperature and can be isolated. The aqueous solution of the salt decomposes to phenol on boiling with water with evolution of N_2 .



iv) Action of oxygen on Grignard reagent followed by hydrolysis:

Just as Grignard reagent adds to CO_2 , aryl Grignard reagents add to molecular oxygen.

The intermediate reacts with another molecule of the Grignard reagent and hydrolysis of the product gives phenol.



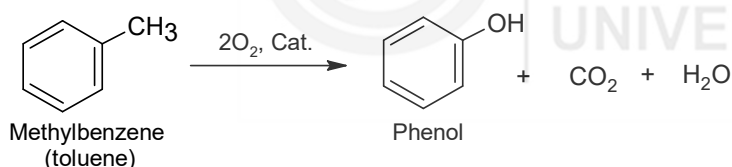
Commercial Preparation

Phenols are of great commercial importance. In this section you will learn how large quantities of these compounds are prepared from different abundant natural sources.

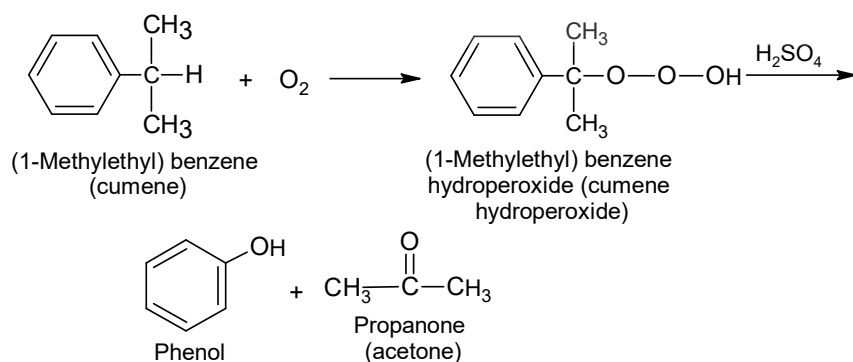
From natural sources: On a commercial scale, phenols are obtained from coal tar. Coal tar is fractionated and the middle oil is cooled when naphthalene crystallises out. The liquid is treated with aqueous sodium hydroxide which dissolves phenols. Carbon dioxide is passed into the liquid and the aqueous layer is separated. Fractionation of remaining oil gives phenol (20%), cresols (43%), xylenols (26%) and the residue is pitch.

From other aromatic hydrocabons:

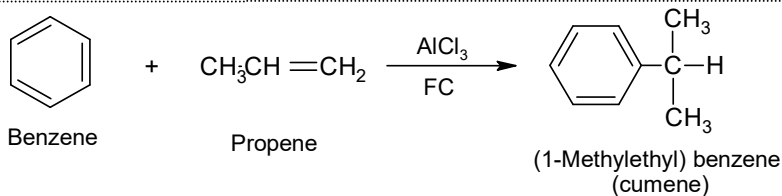
- a) Phenol can be obtained by the catalytic oxidation of methylbenzene (toluene) by air in presence of manganous and cupric salts.



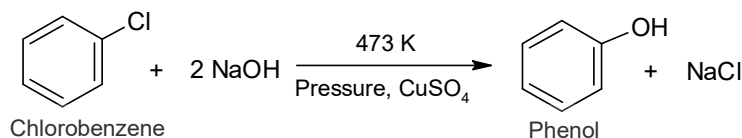
- b) **The cumene process:** (1-Methylethyl) benzene (cumene or isopropylbenzene) is a constituent of crude oil and refined fuels. Oxidation of cumene to hydroperoxide followed by decomposition by acid gives phenol and an important by-product propanone (acetone):



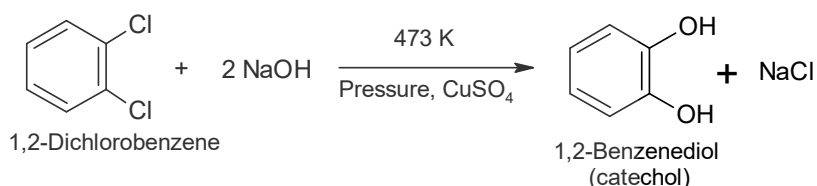
Synthetic cumene is made almost exclusively from benzene and propene via a Friedel-Crafts reaction.



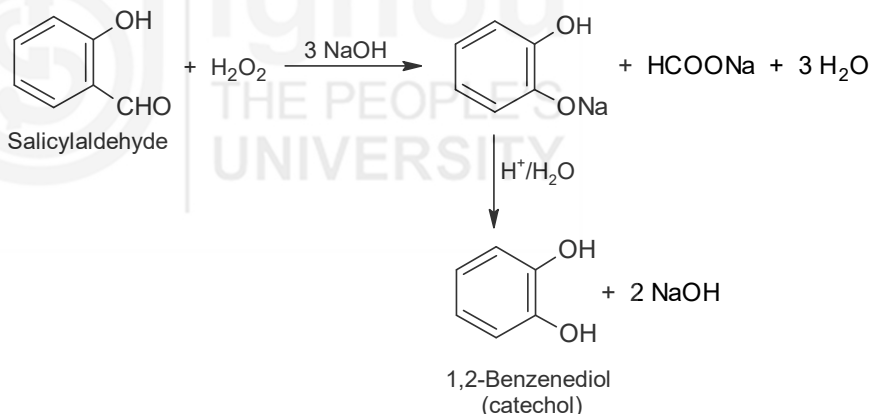
- c) **The Dow process:** Chlorobenzene and sodium hydroxide react at high temperature and under pressure in the presence of a catalyst (copper salts) to give phenols.



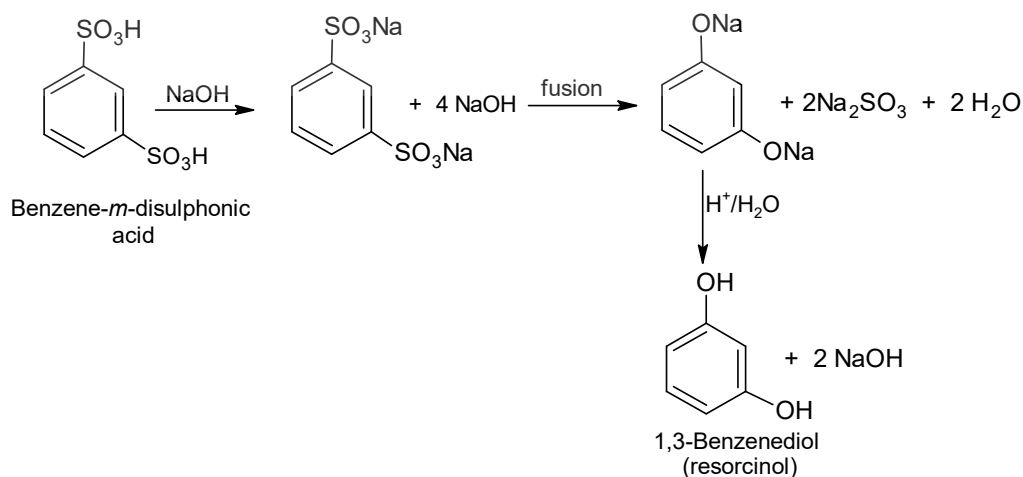
When this process is applied to 1,2-dichlorobenzenes (catechol) is obtained.



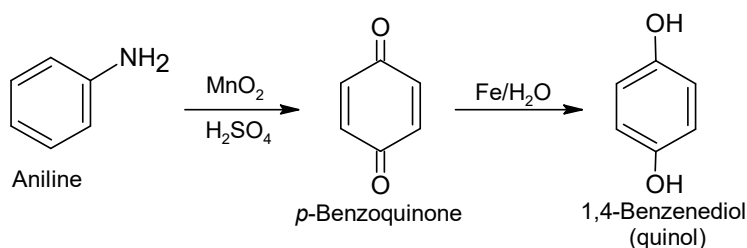
- d) 1,2-Benzenediol (catechol) can be conveniently prepared by the action of alkaline hydrogen peroxide on salicylaldehyde. The reaction is an example of Baeyer-Villiger rearrangement.



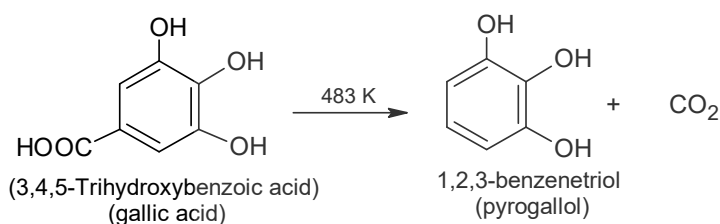
- e) 1,3-Benzenediol (resorcinol) is prepared industrially by the alkaline fusion of benzene *m*-disulphonic acid:



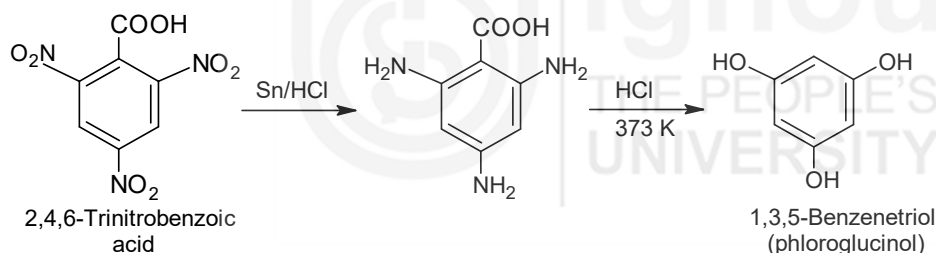
- f) 1,4-Benzenediol (quinol) is made commercially by the oxidation of aniline with manganese dioxide and sulphuric acid. The product *p*-benzoquinone is reduced to quinol with iron and hot water.



- g) 1,2,3-Benzenetriol (pyrogallol) is prepared by heating gallic acid (3,4,5-trihydroxybenzoic acid) in a stream of carbon dioxide or by heating an aqueous solution of gallic acid at 483 K under pressure:

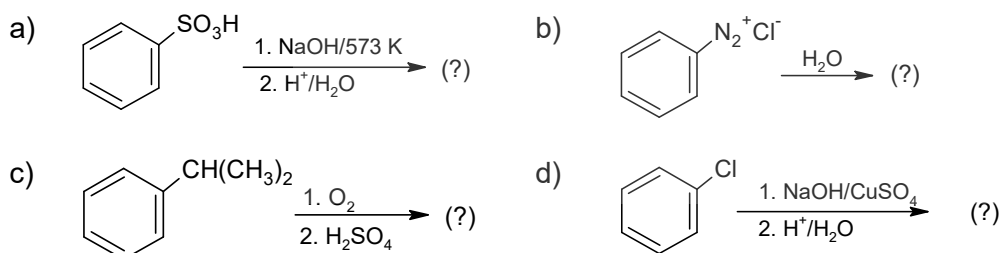


- h) 1,3,5-Benzenetriol (phloroglucinol) is obtained by the fusion of many plant resins with alkali. It is also prepared by the reduction of 2,4,6-trinitrobenzoic acid to the amino derivative followed by reaction with hot hydrochloric acid.



SAQ 4

Complete the following reactions:



SAQ 5

How the following conversion can be carried out?

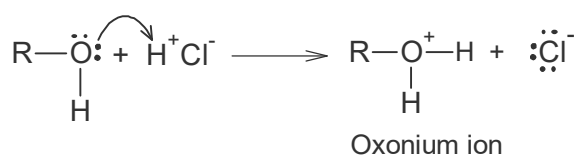
- | | |
|--------------------------------------|------------------------------------|
| a) Benzene to phenol | b) Phenylamine (Aniline) to phenol |
| c) Phenylmagnesium bromide to phenol | d) Chlorobenzene to phenol |

16.5 CHEMICAL PROPERTIES

As stated earlier, phenols have very different chemical properties compared to alcohols. One of the most important differences is that phenols are significantly more acidic than alcohols. Therefore, it is worth comparing the acidity of alcohols and phenols and the effect of substituents on it before further going in details of various types of chemical reactions of phenols.

16.5.1 Acidity and Basicity of Alcohols and Phenols

Alcohols are neutral towards litmus. But in their reactions they behave both as an acid and as a base depending upon the reaction conditions. For example, in acidic solution, alcohols are protonated and thus the acid-base equilibrium with alcohol acting as a base is established. It is the same type of reaction that occurs between water and an acid. A protonated alcohol molecule is called an oxonium ion.

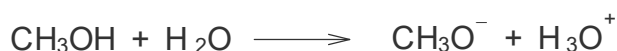


An alcohol can also lose a proton to a strong base yielding an alkoxide ion, RO^- . In this reaction, the alcohol behaves as an acid.

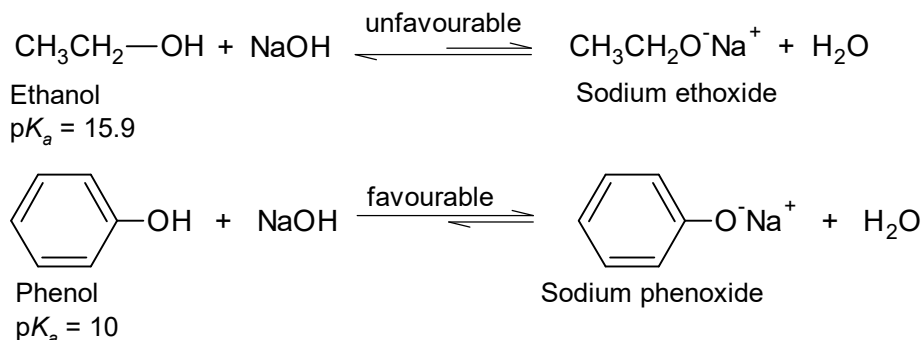
Alkoxides are strong bases, generally stronger than hydroxides. To prepare an alkoxide from an alcohol, we need a base stronger than the alkoxide itself, such as, alkali metal hydrides, NaH , KH , etc.



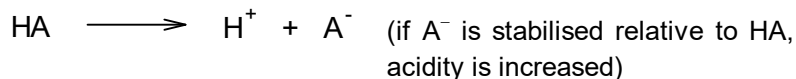
In dilute aqueous solutions, alcohol has approximately same $\text{p}K_a$ values as water. For example, the $\text{p}K_a$ of methanol in water is 15.5, while that of pure water is 15.74. Therefore it is as acidic as water.



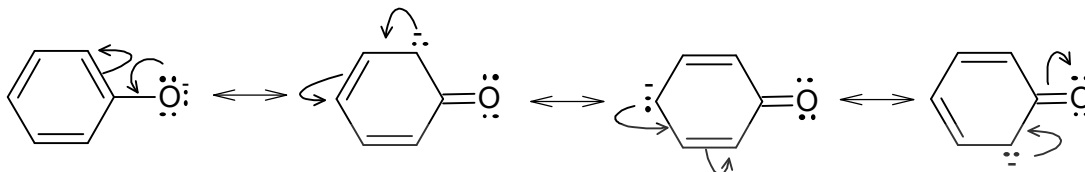
On the other hand, phenols are distinctly acidic in character. Phenol, with a $\text{p}K_a$ of 10.00 is a stronger acid than an alcohol or water. Unlike alkoxide ion of alcohols, the phenoxide ion (ArO^-) is a weaker base than OH^- . Therefore, a phenoxide can be prepared by treatment of the phenol with aqueous sodium hydroxide.



degree of ionisation of a weak acid is determined by the relative stabilities of the unionized compound and the anion:



The reason for the greater acidity of phenol compared to that of alcohol is that the ionised product is resonance stabilised, with the negative charge delocalised by the aromatic ring.

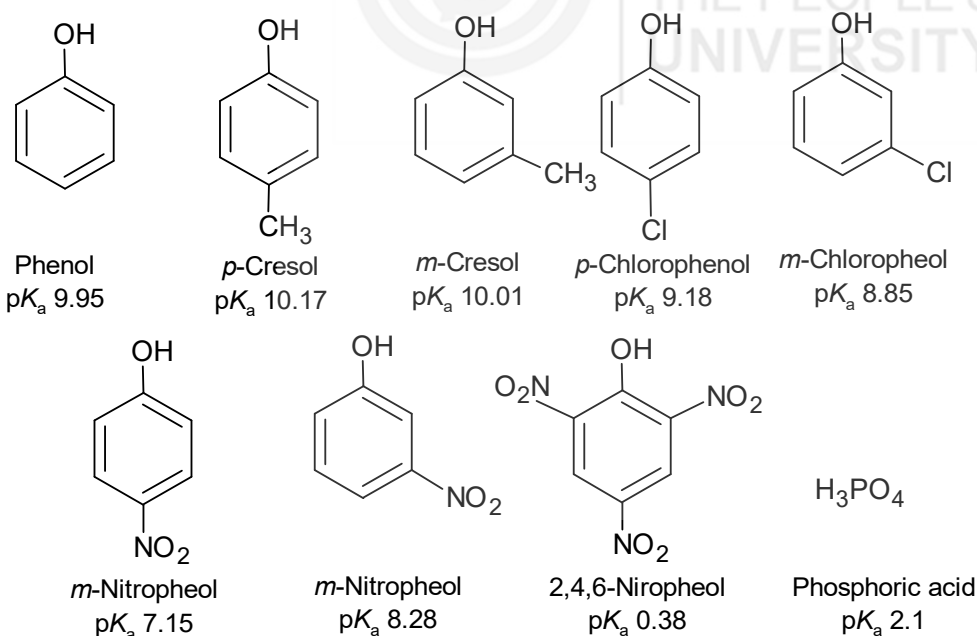


The negative charge in an alkoxide ion (RO^-) cannot be delocalised. Therefore, alkoxide ion is of higher energy relative to the alcohol, and as a result, alcohols are not as strong acid as phenols. Further, the alkyl group in the alkoxide ion has a destabilising effect because of positive inductive (+I) effect (electron releasing effect) of the alkyl group. Therefore, addition of alkyl groups to the α -carbon decreases the acidity of alcohols. We can now write the order of decreasing acid strength.

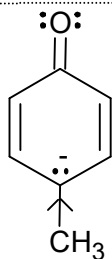
+ I effect of alkyl group further increase the intensity of negative charge on oxygen of alkoxide ion; thus destabilises the alkoxide ion.



In phenols, substituents located ortho or para to the $-\text{OH}$ group, can dramatically influence the acidity of the phenol due to a combination of inductive and resonance effects. The electron withdrawing groups enhance the acidity while the electron donating substituents decrease the acidity.

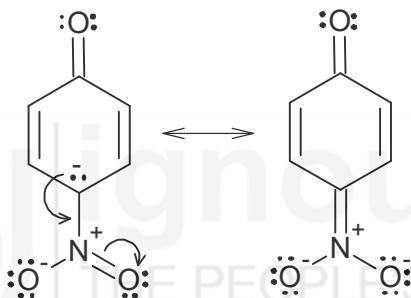


The acid-weakening effect of alkyl substituents can be understood in the following way. The +I effect of alkyl substituents are due to the higher electronegativity of sp^2 hybridised carbon of aromatic ring than sp^3 -hybridised atom of an alkyl group. Thus, alkyl substituents are electron releasing towards the aromatic ring. Because of electron releasing effect of alkyl substituent, it will destabilise phenoxide ion contributing structures and in effect reduce the acidity of alkyl substituted phenol.



The +I inductive effect of methyl group destabilises this contributing structure

Halogens have $-I$ effect as they are more electronegative than carbon, they withdraw electron density from the aromatic ring and thus stabilise the halophenoxide ion compared to phenoxide ion. As fluorine is most electronegative among halogens, the fluorophenol will be the most acidic. This effect will be less for chlorophenol and still less for bromophenol. In the case of nitrophenol both the inductive and resonance effects are observed. Therefore, these phenols are highly acidic. 2,4,6-trinitrophenol (picric acid) is a stronger acid than phosphoric acid. In the case of nitrophenols, if nitro group is ortho or para to hydroxyl group, it further contributes in negative charge delocalisation as shown by following contributing structure on the right.



Delocalization of negative charge onto oxygen further increase the resonance stabilization of phenoxide ion

Furthermore phenols, like alcohols, can be protonated by strong acids to give the corresponding oxonium ions. Also, similar to alcohols, the hydroxy group of phenols has amphoteric character. However, the basicity of phenols is even less than that of the alcohols, because the lone electron pairs on the oxygen are delocalised into benzene ring.

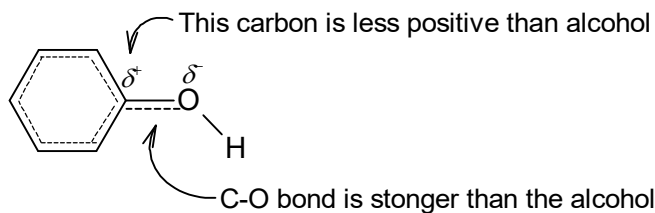
SAQ 6

4-Hydroxybenzaldehyde (*p*-hydroxybenzaldehyde) is more acidic ($pK_a = -7.3$) than phenol ($pK_a = 9.89$). Explain.

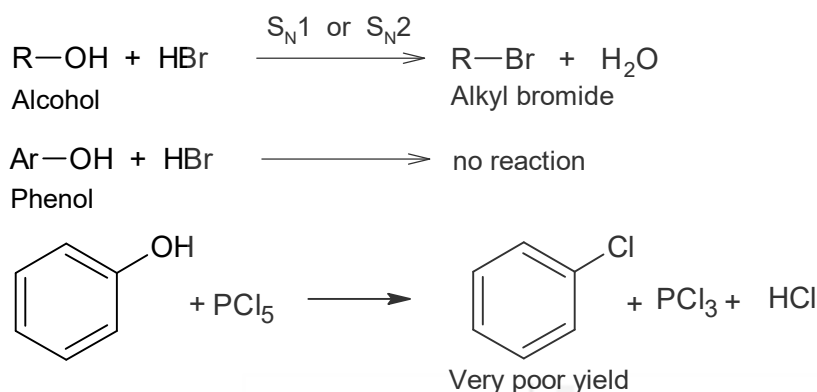
16.5.2 Reactions of Phenols

In phenols, as mentioned earlier, the hydroxyl group is attached to an sp^2 hybridised carbon of aromatic ring and the carbon oxygen bond of phenols has considerable double bond character as evident from the resonance structures shown for the delocalisation of lone pair of oxygen. Due to these factors, the bond is shorter and stronger than a carbon oxygen single bond. As hydroxyl group bonded to an aromatic ring is held tightly, therefore breaking up of the C – O bond is very difficult. Consequently, the nucleophilic substitution and

elimination reactions so typical of an alcohol are generally not observed for a phenol. Nucleophilic substitution on carbon atom of carbon oxygen bond is also discouraged by the delocalisation of the positive charge created by more electronegative oxygen over benzene ring.



For example, hydrogen halides do not react at all with phenol and even phosphorus pentachloride produces only a poor yield of chlorobenzene.



Somehow hydroxyl group can be removed by distillation of phenol with Zinc dust, but in this case again yield is very poor. Free radical mechanism is involved in this reaction.

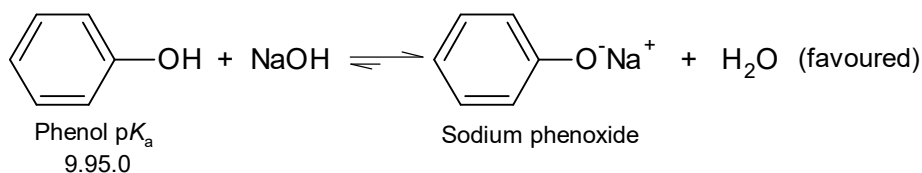
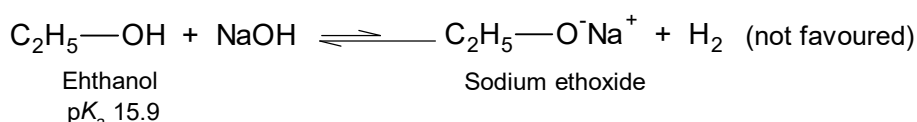


Phenols exhibit reactions mainly due to the phenolic hydroxy group and the aromatic ring.

With this background, now let us study the reactions of phenols.

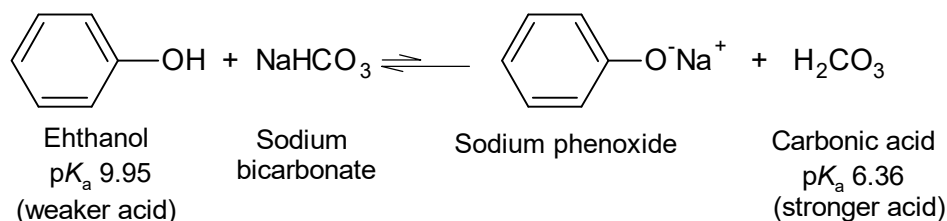
16.5.3 Reactions due to Phenolic Hydroxyl Group

- i) **Formation of phenoxides:** We have already mentioned that phenols are weak acids. They react with strong alkalis forming phenoxides and water. This reactivity is in direct contrast to that of alcohols. We have seen that alcohols form alkoxide only with strong bases like NaH and metals like Na, K, Mg, etc.



Phenol is about 1 million times more acidic than alcohols. However, phenol is not as strong an acid as carbonic acid or a carboxylic acid. This affords a method for distinguishing phenol from a carboxylic acid. Phenol does not react with an aqueous solution of sodium bicarbonate, whereas carboxylic acid reacts to liberate carbon dioxide. The separation of a mixture of phenol and a carboxylic acid is based on the same principle.

Carbonic acid is a stronger acid than phenol, therefore the equilibrium for the reaction of phenol and bicarbonate ions lies far to the left.

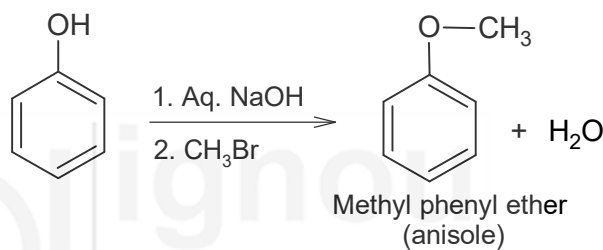


Therefore, phenol does not react with an aqueous solution of sodium bicarbonate, whereas carboxylic acid reacts to liberate carbon dioxide.



Again recall from earlier discussion that phenols are stronger acids than alcohols as the phenoxide ion is stabilised by resonance. No such stabilisation is possible in the case of alkoxide ions.

ii) **Alkylation:** Similar to alcohols, phenols undergo reaction with alkyl halide (Williamson ether synthesis) in presence of base.

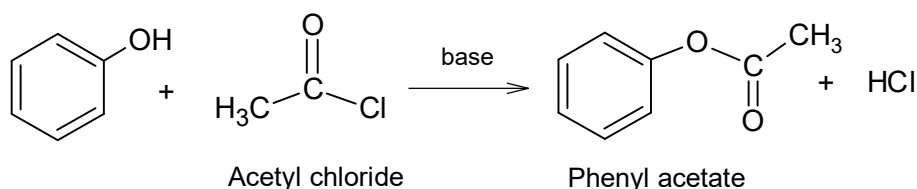


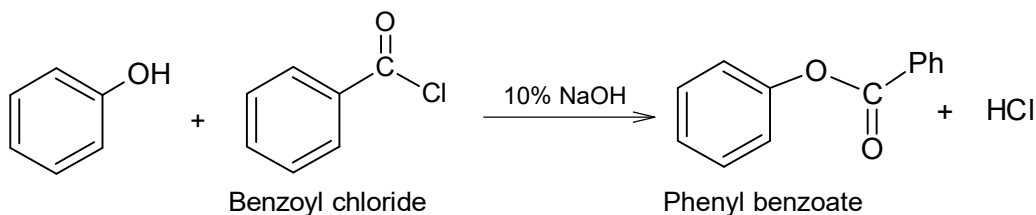
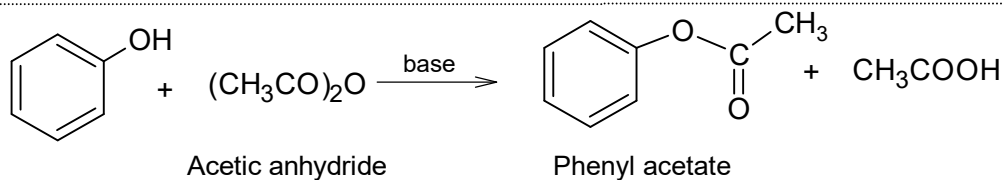
The reaction follows the S_N2 mechanism



iii) **Esterification:** Unlike alcohols, phenol reacts slowly with carboxylic acids that we normally carry out its esterification with acyl halides (acid halides) or acid anhydrides instead.

Phenols react with acyl halides or anhydrides in presence of a base such as pyridine or NaOH to form esters. These reactions can be done under milder conditions than those used for alcohols due to the greater acidity of phenols as we have seen that phenols can be converted to phenoxide ions with sodium hydroxide rather than very strong bases or metallic sodium. It is important to note that phenoxide which formed in basic reaction conditions is a better nucleophile than phenol. Thus, the presence of base facilitates the ester formation.





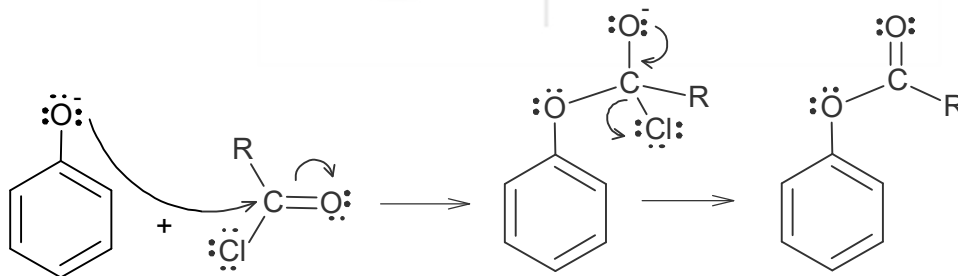
The reaction of phenols with benzoyl chloride in presence of 10 % NaOH is known as **Schotten-Baumann reaction**. Unlike alcohols, esterification of phenol does not occur with a carboxylic acid under acid catalyst as poor availability of lone pairs of phenolic group for nucleophilic attack on the carbon atom of carboxylic group.

Mechanism: Esterification of phenol is an example of nucleophilic acyl substitution reaction.

Step 1: Formation of phenoxide ion



Step 2: Phenoxide ion (as nucleophile) attacks on carbonyl carbon of acyl chloride and replaces chloride ion (Addition elimination).



iv) Reaction with Iron(III) Chloride: Phenols produce coloured complexes when mixed with iron(III) chloride since phenols act as ligands in such reactions. These reactions are often used as a test for phenols.

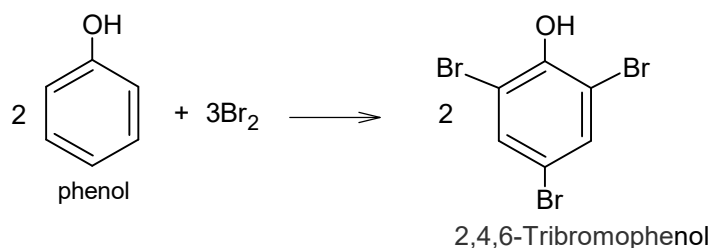
SAQ 7

Discuss the role of base in estrification reactions.

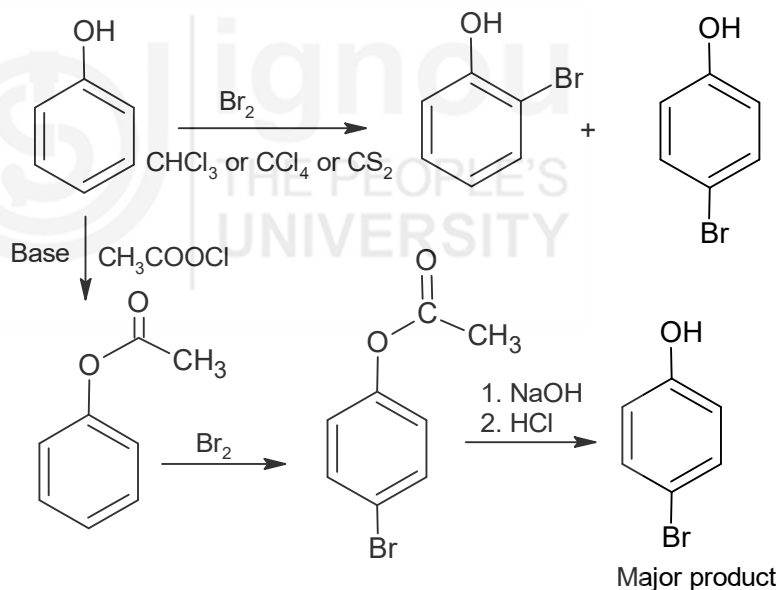
16.5.4 Reactions due to Aromatic Ring

As we mentioned earlier, the -OH group is a powerful activator in electrophilic aromatic substitution reactions and directs substitution to the ortho and para positions. Therefore, phenol is much more reactive towards electrophilic substitution reactions than benzene.

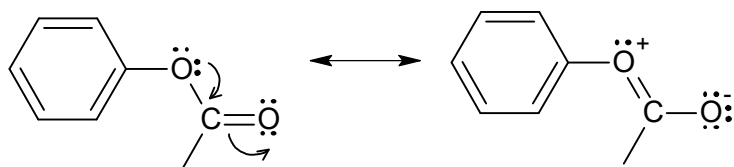
- i) **Electrophilic aromatic substitution reaction:** Phenol undergoes electrophilic substitution quite readily. Sometimes phenolic group can be too powerful activating group and it is difficult to control the reaction to one substitution. For example, on shaking phenol with bromine water at room temperature, 2,4,6-tribromophenol is formed:



The activating power of phenolic group can be decreased by carrying out reaction in less polar or nonpolar solvents such as CHCl_3 , CCl_4 or CS_2 etc.. This is because, in more polar solvent such as water, phenol is available mainly in the form of phenoxide ion (PhO^-) which is more reactive than Phenol. On the other hand, in less polar solvent, phenol form dominates. Other way is by converting the phenol to ester that can be removed by hydrolysis once electrophilic substitution has been carried out. Since the ester is weak activating group and also bulky, it will discourage ortho attack and para product will be the major product.

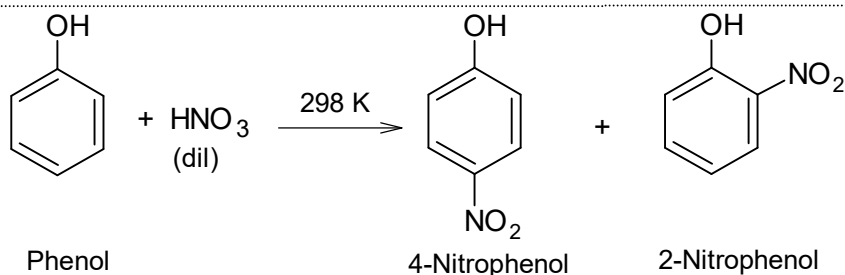


Following resonating structures explain less reactivity of phenyl acetate (acetoxybenzene):

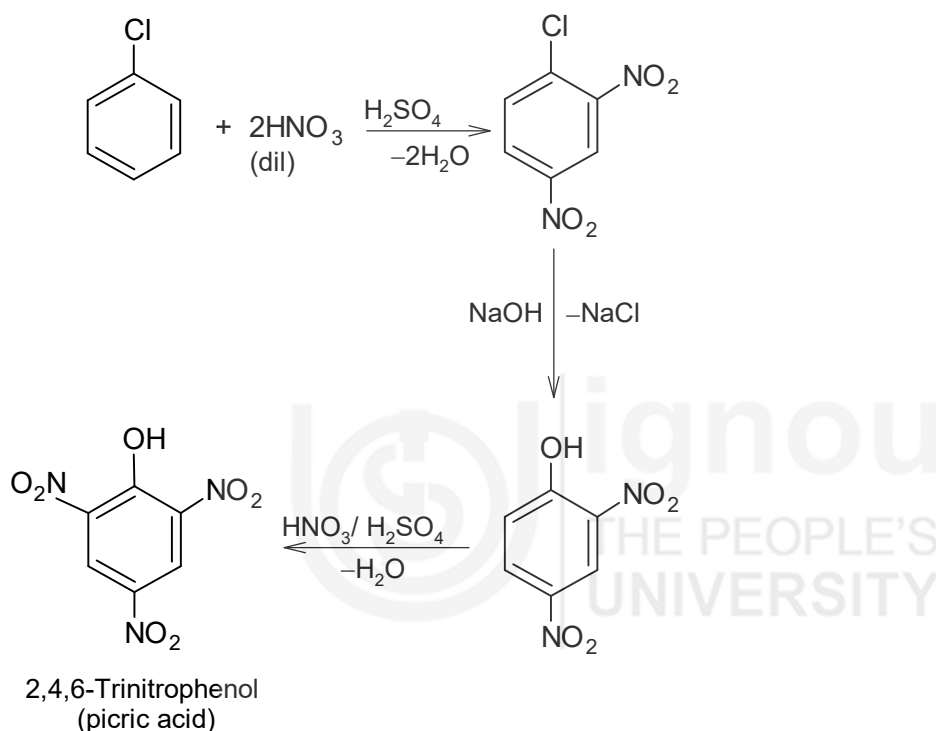


Due to these resonating structures, oxygen electrons are less available to ring

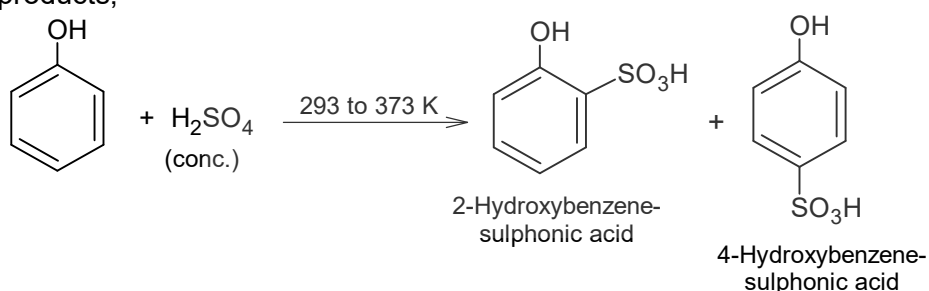
On treatment with dilute nitric acid, phenol gives *o*- and *p*-nitrophenols. Unlike nitration of benzene, there is no need of nitration mixture (conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4$) because of high reactivity of phenol.



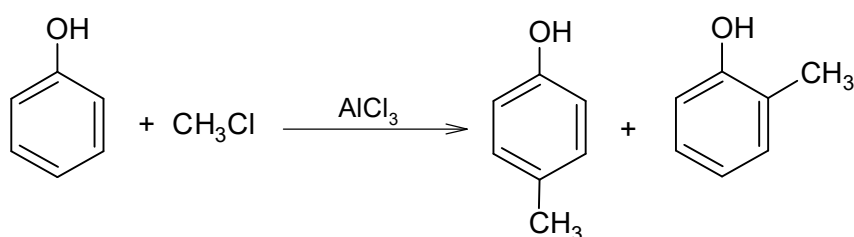
Phenol, when nitrated directly with concentrated nitric acid, undergoes oxidation. For this reason, 2,4,6-trinitrophenol (picric acid) is obtained through a synthesis that begins with chlorobenzene. The first product is 2,4-dinitrochlorobenzene, which is then easily hydrolysed to, 2,4-dinitrophenol and the nitration continued to give picric acid in good yield.

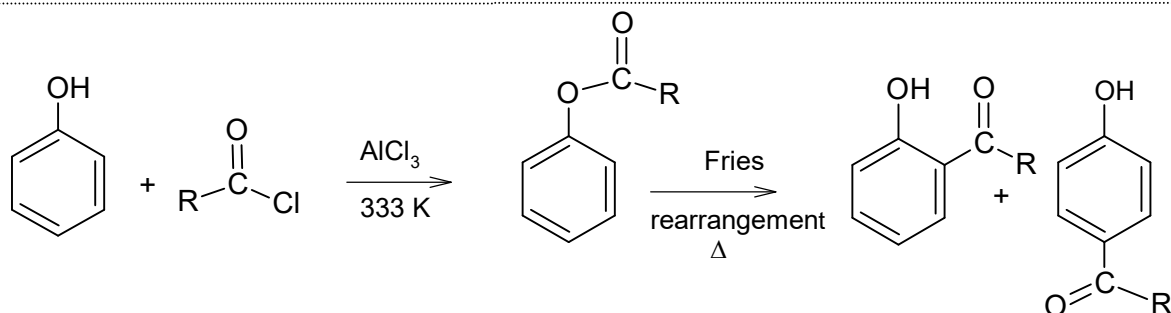


Phenol, when treated with sulphuric acid, yields both ortho and para products,

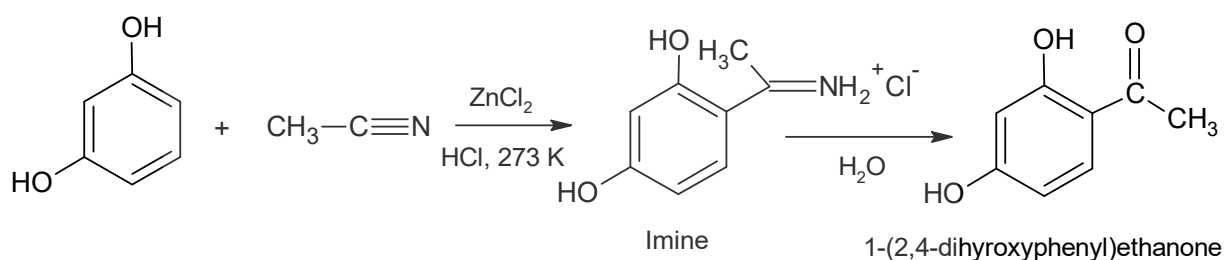


Phenol can easily undergo Friedel-Crafts alkylation or acylation. Acylation products in presence of AlCl_3 undergo Fries rearrangement.

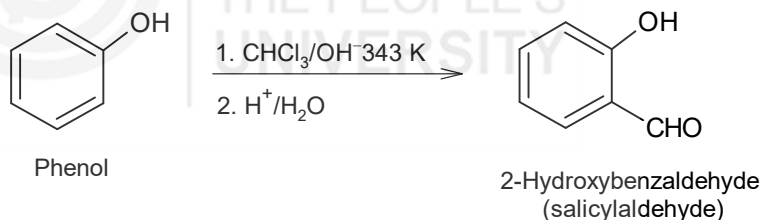




Similar to Friedel-Crafts acylation, acylation of phenol can also be carried out with organic nitriles in presence of hydrogen chloride gas and Lewis acid catalyst (e.g. ZnCl_2 , FeCl_3 , AlCl_3 etc.). This reaction is known as Hauben-Hoesch reaction. This reaction has been found to be very useful with polyhydroxy phenol. In this reaction, phenol gives imine as intermediate product which on hydrolysis gives aryl ketone.

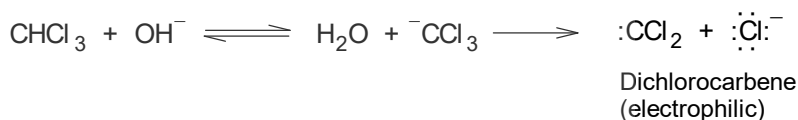


- ii) **Reimer-Tiemann reaction:** Phenols undergo the Reimer-Tiemann reaction. In it an alkaline solution of phenol is heated with trichloromethane (chloroform) and the product is acidified to give 2-hydroxybenzaldehyde (salicylaldehyde).

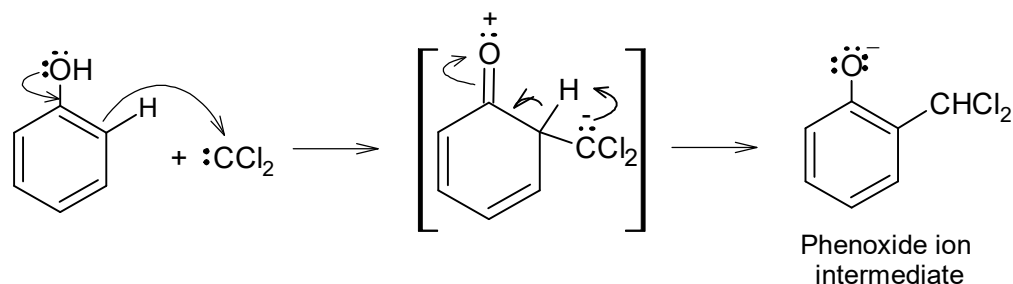


Mechanism: Reimer-Tiemann Reaction

Step 1: Formation of electrophilic dichloro carbene

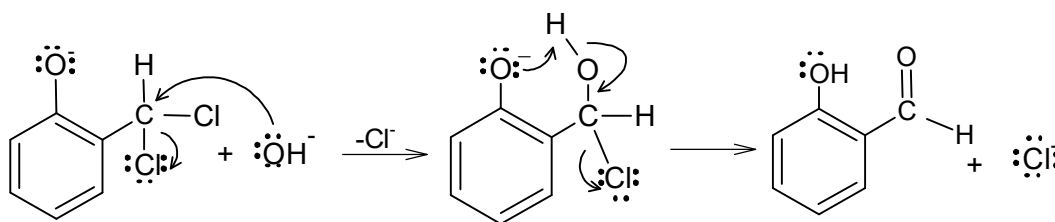


Step 2: Electrophilic addition of carbene to phenol.

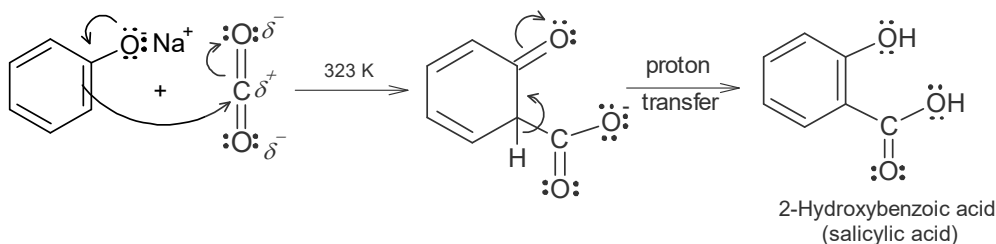


Step 3: Phenoxide formed in Step 2 reacts with strong base to form

2-hydroxybenzaldehyde.



- iii) **Kolbe reaction:** On heating sodium or potassium phenoxide with carbon dioxide and subsequent acidification, 2-hydroxybenzoic acid (salicylic acid) is formed. This is known as **Kolbe reaction**. In this reaction, carbon of CO_2 acts as an electrophile in aromatic substitution.



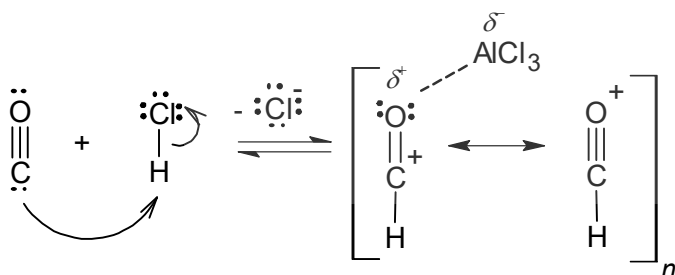
- iv) **Gattermann and Koch formylation:** The introduction of a formyl group into electronic rich aromatic rings by using CO/HCl /Lewis acid catalyst (AlCl_3 , AlBr_3 , FeCl_3 etc.) is known as Gattermann-Koch formylation. Co-catalyst such as Cu_2Cl_2 , TiCl_4 or NiCl_2 is needed to carry out reaction at normal atmospheric pressure; however, no catalyst is needed at high pressure (100-250 atm).

Gattermann introduced a modification where HCN is mixed with HCl in presence of ZnCl_2 to formylate phenols. This modification is called the Gattermann formylation or Gattermann synthesis. Formylation generally occurs *para* to hydroxyl groups. Both these reactions belong to the category of electrophilic aromatic substitution.

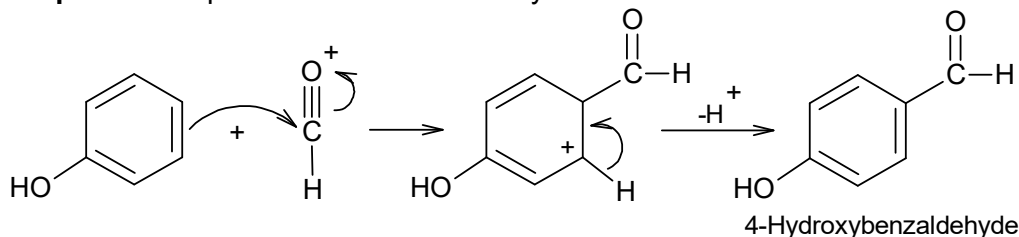
As HCN is very toxic compound so R Adams suggested modification for the Gattermann synthesis. He generated HCN during reaction (in situ) by the reaction of $\text{Zn}(\text{CN})_2$ with HCl .

Mechanism: Gattermann-Koch Formylation

Step 1: Formation of formylation

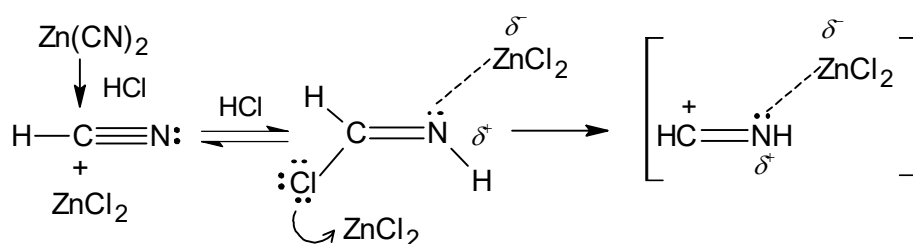


Step 2: Electrophilic substitution of formyl cation

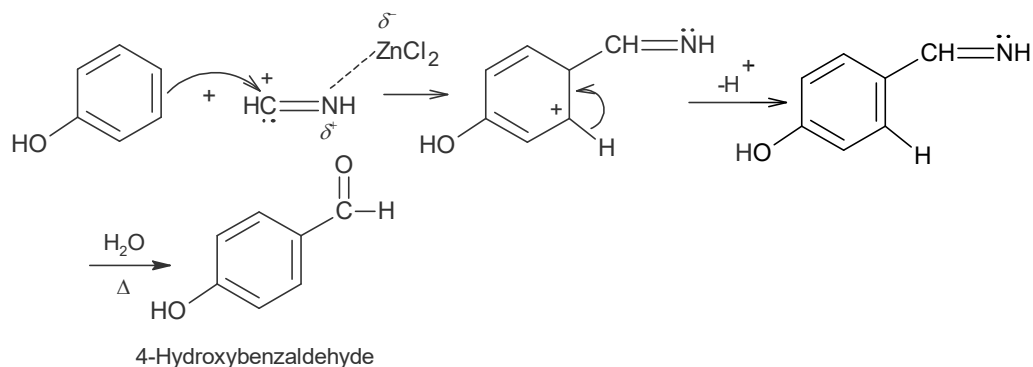


Gattermann Synthesis

Step 1: Formation of electrophilic $[^+CH=NH]$



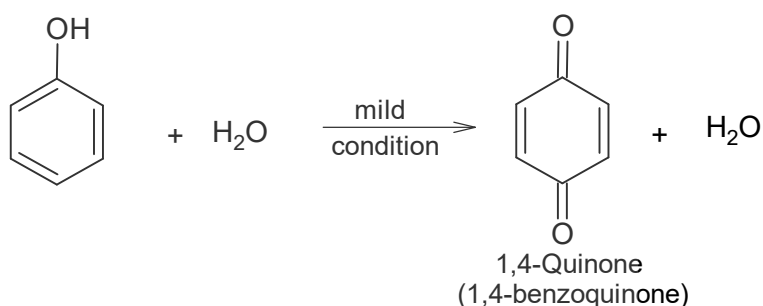
Step 2: Electrophilic substitution of $[NC^+=NH]$



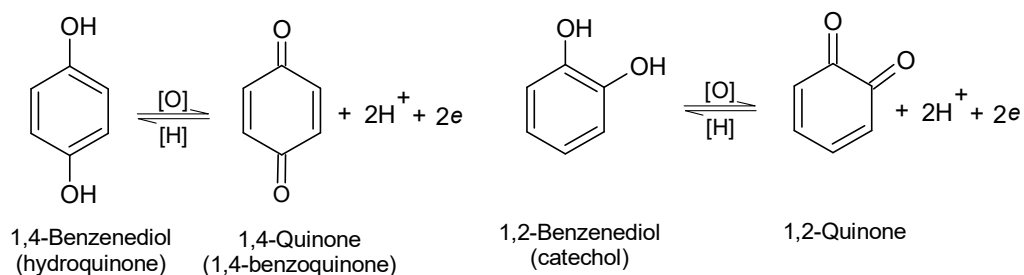
16.5.4 Oxidation of Phenols

The ability of hydroquinone to reduce silver ions to silver metal is the chemical basis of photography. Hydroquinone is developer fluid which reduces the light activated silver ions at a faster rate than the nonexposed silver ions. In the fixing process unreacted silver halide is converted into a water soluble silver complex of sodium thiosulphate, and washed from film. The result is the familiar photographic negative.

Phenols are easily oxidised, but their products are often complex. The oxidation may occur with air alone (**autoxidation**) or with other oxidising agents. The reaction of phenols with oxygen in the air is exploited industrially by the use of phenol as antioxidants in gasoline, rubber and other products. Phenols react with oxygen more readily than most other organic compounds and protect them from oxidation.



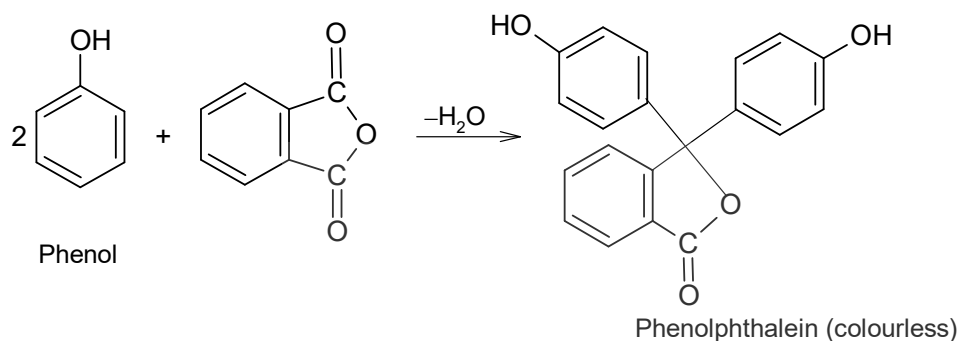
Hydroquinone and catechol are easily oxidised to quinones by mild oxidising agents such as Ag^+ or Fe^{3+} .



16.5.5 Condensation Reactions

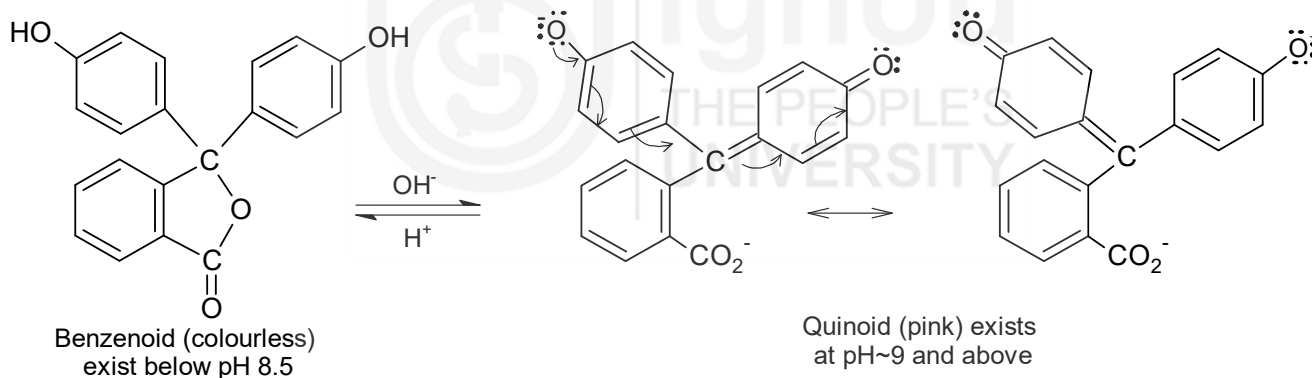
Condensation of phenols with phthalic anhydride in the presence of a dehydrating agent gives a class of compounds known as **phthaleins**. These are dyes.

By heating a mixture of phenol and phthalic anhydride in the presence of concentrated sulphuric acid, phenolphthalein is formed:



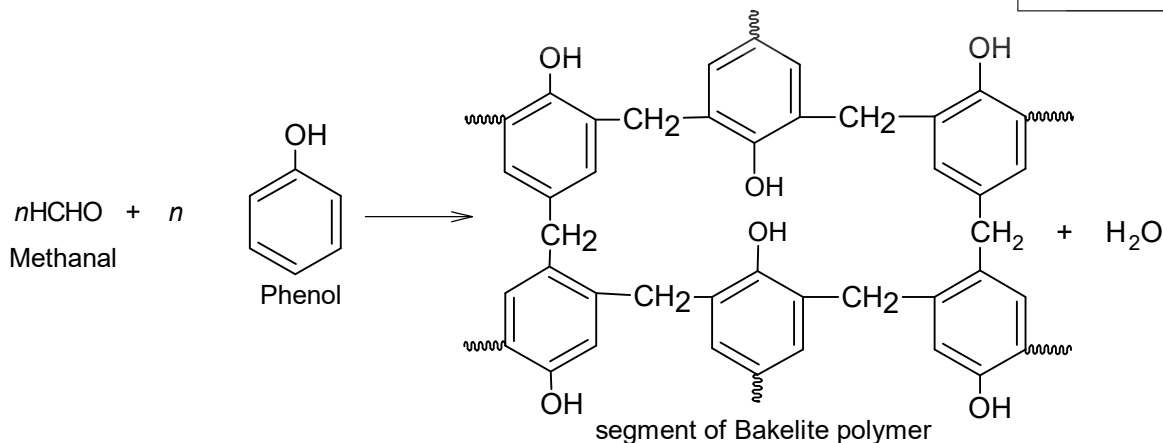
Phenolphthalein is colourless in acidic medium. On addition of alkali, a pink coloration develops due to the quinoid form. Addition of excess alkali regenerates the benzenoid structure which is colourless. Phenolphthalein is commonly used in the laboratory as a pH indicator. At pH below 8.5, the molecule exists in colourless form and at pH~9 and above, in pink form.

Phenolphthalein as pH indicator



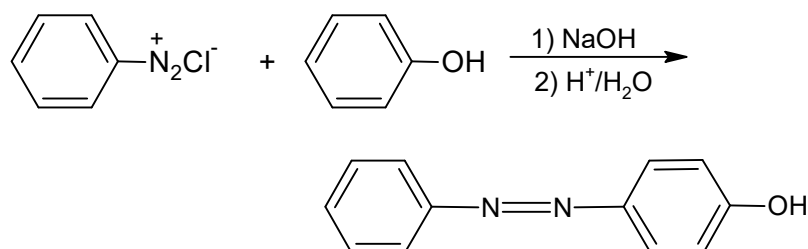
The condensation of phenol with excess of methanal (formaldehyde) in the presence of dilute sodium hydroxide gives polymer which is known as Bakelite. These are phenol methanol (phenol-formaldehyde) resins which are three-dimensional polymer of the following possible structure:

The electric resistance of Bakelite makes it especially useful for electric plugs, switches and tools.



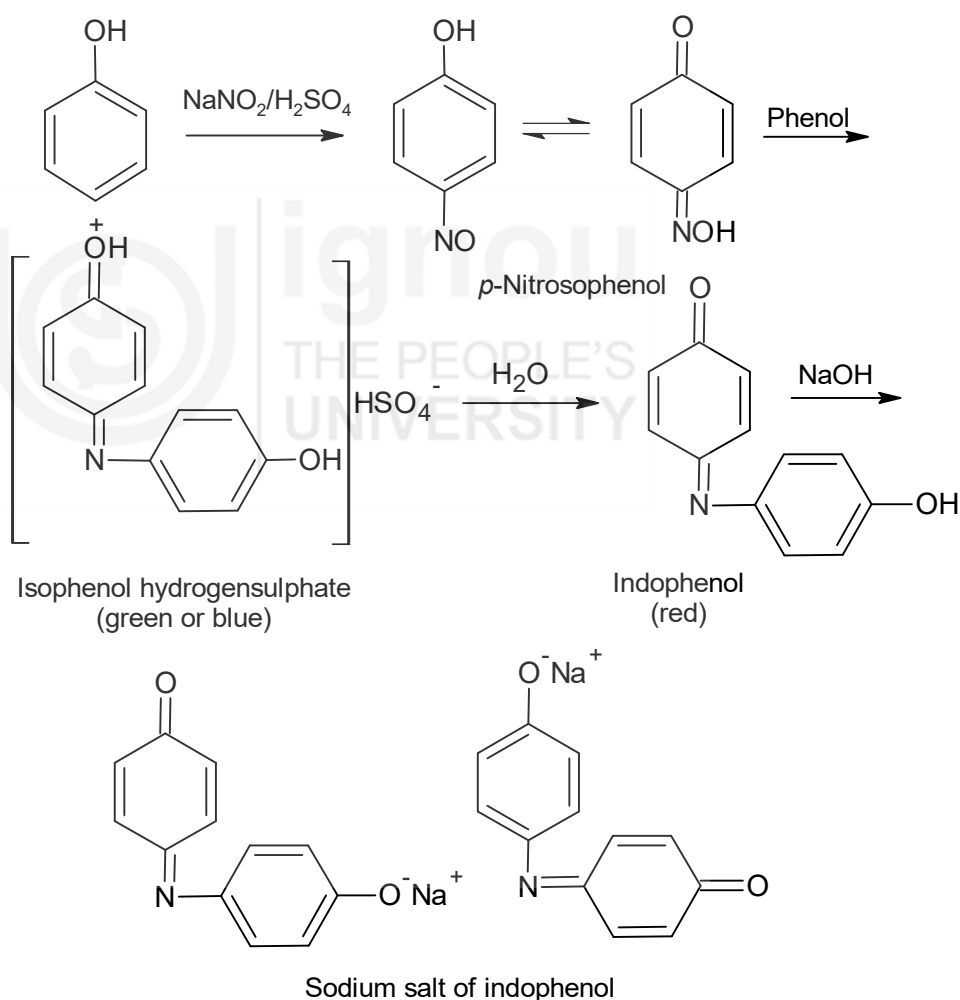
16.5.6 Coupling Reaction

Phenols couple with diazonium salts in alkaline conditions to form azo dyes. This reaction follows electrophilic substitution mechanism.



16.5.7 Libermann's Nitroso Reaction

Phenol reacts with sodium nitrite and concentrated sulphuric acid and forms a green or blue coloured complex. This blue colour of complex changes to red on dilution. The red colour of complex change to blue, if we change the acidic medium to alkaline.



SAQ 8

Treatment of phenol with trichloromethane (chloroform) and aqueous sodium hydroxide gives:

- | | |
|--------------------------|--------------------------|
| a) 2-chlorophenol | b) 2-hydroxybenzaldehyde |
| c) 3-hydroxybenzaldehyde | d) 3-chlorophenol |

SAQ 9

How will you bring about following conversions?

- a) Phenol to phenyl benzoate b) Phenol to 4-hydroxybenzaldehyde
c) Phenol to 4-bromophenol d) Chlorobenzene to picric acid
-

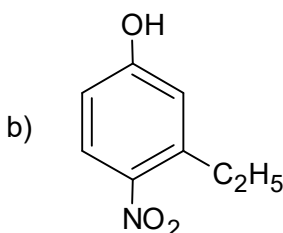
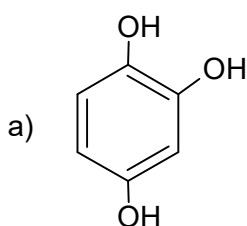
16.6 SUMMARY

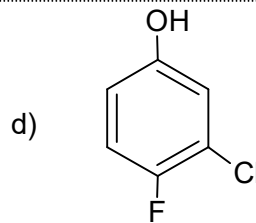
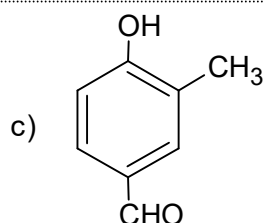
In this unit we have described the chemistry of phenols. We are summarising below what we have studied:

- Phenols are polar compounds and the –OH group of phenols participates in hydrogen bonding. Therefore, the boiling points and melting points of phenols are higher than aryl halides.
- Phenols are obtained by the decarboxylation of phenolic acid, action of water on diazonium salts and from Grignard reagent. They are prepared on a commercial scale by catalytic oxidation of methylbenzene (toluene) or decomposition of cumene peroxide or from chlorobenzene by Dow process. Phenols are also obtained from coal tar.
- Phenols are stronger acids than alcohols. They are easily converted to phenoxide ions on treatment with aqueous sodium hydroxide.
- Electron releasing substituents attached to the ring, decrease acidity of phenols. Strongly electron withdrawing groups such as –NO₂ at ortho and para positions increase the acidity many fold.
- The –OH group of phenol is powerful activator substituent and electrophilic aromatic substitution occurs readily in phenols.
- Phenol undergoes electrophilic substitution (nitration, halogenation, Friedel-Crafts reaction, sulphonation, etc.) quite readily giving a mixture of ortho- and para-derivatives.
- On heating phenol with trichloromethane (chloroform) and potassium hydroxide, 2-hydroxy benzaldehyde is obtained. On passing carbon dioxide in a mixture of phenol and aq. sodium hydroxide, o-hydroxy benzoic acid is formed.
- On condensation with phthalic anhydride in the presence of a dehydrating agent, phenol gives phthalein dyes. With methanal, phenol gives a polymer, Bakelite.

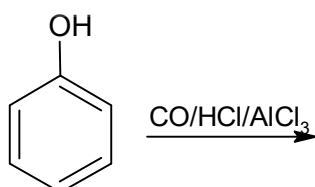
16.7 TERMINAL QUESTIONS

1. Name the following compounds:





2. Write chemical reaction for each of the following reactions.
 - a) Sodium salicylate + soda lime
 - b) Benzene + propene + AlCl_3 + Heat
 - c) 1,2-Dichlorobenzene + NaOH + CuSO_4 + Heat
 - d) Phenyldiazonium salt + H_2O
3. Which compound in each of the following pairs is more acidic? Explain
 - a) Cyclohexanol or phenol;
 - b) 2,4-Dinitrophenol or 3,5-dinitrophenol;
 - c) *p*-Nitrophenol or *m*-nitrophenol;
 - d) 4-Hydroxybenzaldehyde or phenol.
4. Write the mechanism of the formation of salicylic acid from phenol.
5. How will you bring about following conversions?
 - a) Phenol to anisol
 - b) 1,4-Benzenediol to 1,4-quinone
 - c) Phenol to monosubstituted bromophenol
 - d) 1,3,5-benzenetriol to 1-(2,4,6-trihydroxyphenyl)ethanone
 - e) Phenyl acetate to 1-(2-hydroxyphenyl)ethanone.
6. Identify compounds A to C in the synthetic sequence given below:
 - i) Phenol + $\text{CH}_3\text{COCl} \xrightarrow{\text{NaOH}}$ A
 - ii) $\text{A} + \text{Br}_2 \longrightarrow \text{B}$
 - iii) $\text{B} + \text{HCl} \xrightarrow{\Delta} \text{C}$
7. Write all the steps involved in following reaction:

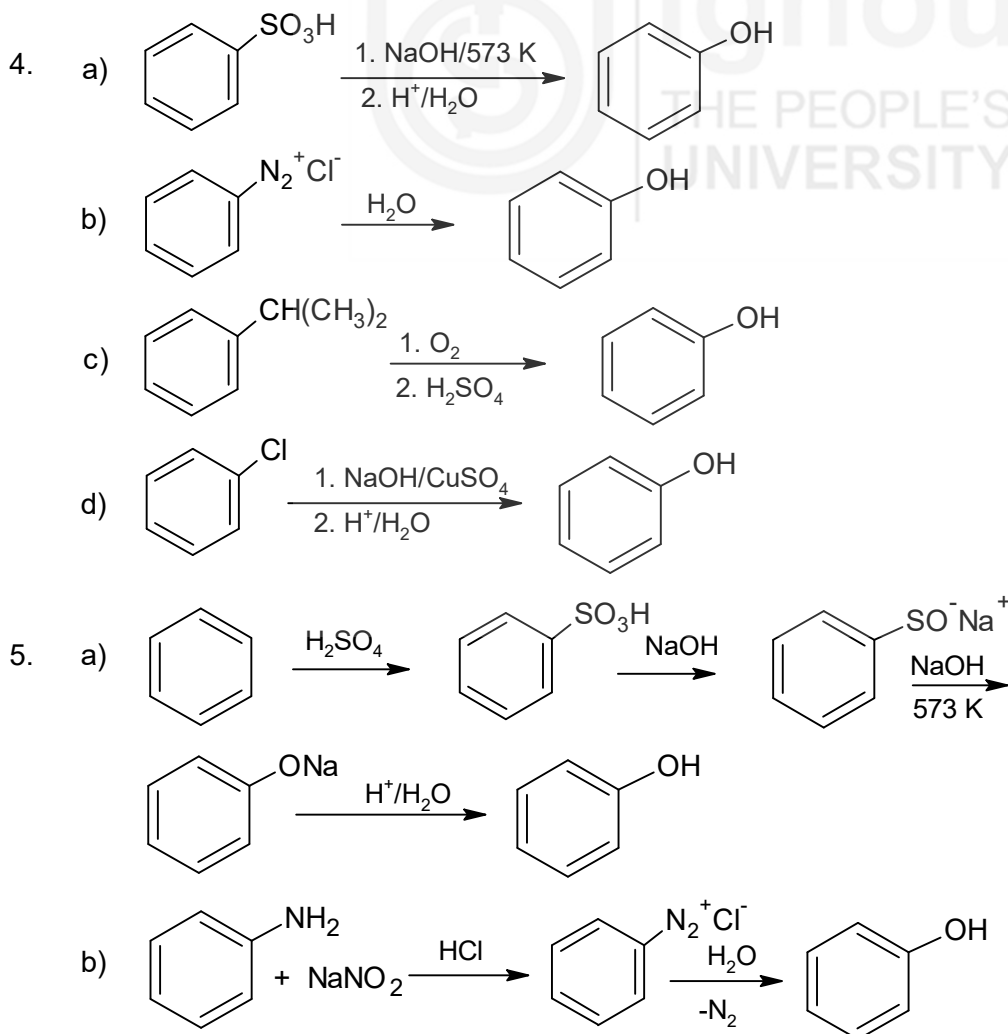


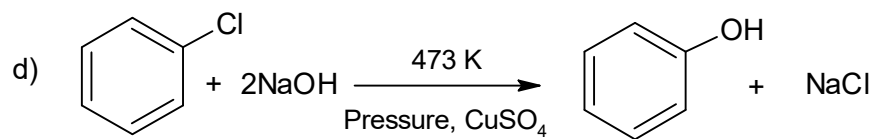
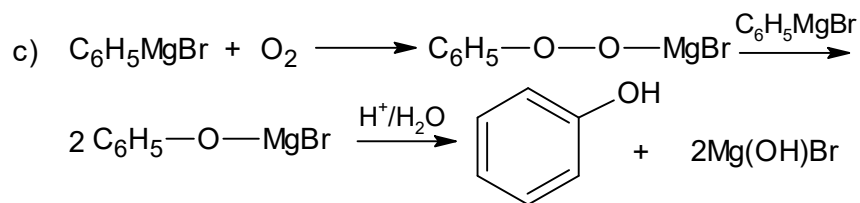
8. How will you test the presence of phenolic group?
9. Outline a reasonable preparation route of following:
 - a) 2,4,6-Trinitrophenol from chlorobenzene
 - b) 4-Nitrophenyl phenyl ether from chlorobezene and phenol.

16.8 ANSWERS

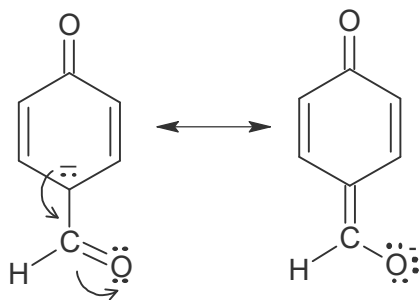
Self Assessment Questions

- 3-Methyl benzenol (*m*-cresol)
 - 3-Hydroxybenzaldehyde (*m*-hydroxybenzaldehyde)
 - 4-Hydroxy-3-methylbenzoic acid
 - 2-Hydroxy-3-methoxybenzoic acid
 - 2-Fluoro-4-hydroxybenzoic acid
- Two factors are mainly responsible for this, These are
 - C-O bond is formed by the overlapping of sp^2 orbital of carbon of benzene ring which has more s character and sp^3 of oxygen atom.
 - The lone pairs on the oxygen atom on phenol can overlap with the delocalised ring system of benzene.
- In case of *o*-fluorophenol, fluorine atom is more electronegative than hydrogen atom of hydroxyl group attached to aromatic ring. This leads to intra-molecular hydrogen bonding within a single molecule. On the other hand, *p*-fluorophenol has intermolecular hydrogen bonding. Therefore, *o*-fluorophenol has lower melting point than *p*-fluorophenol.



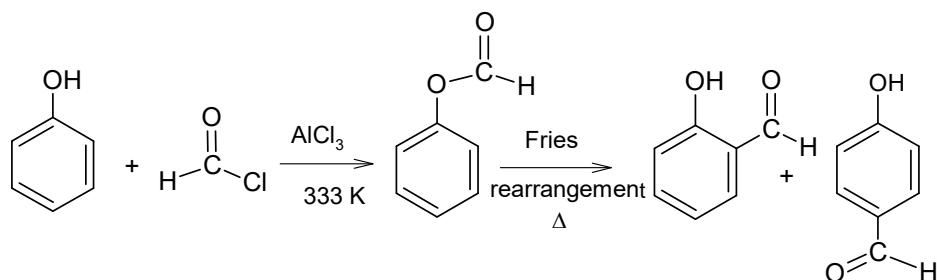
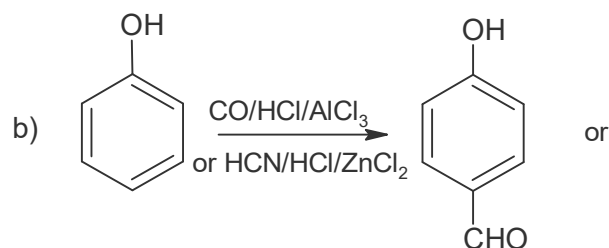
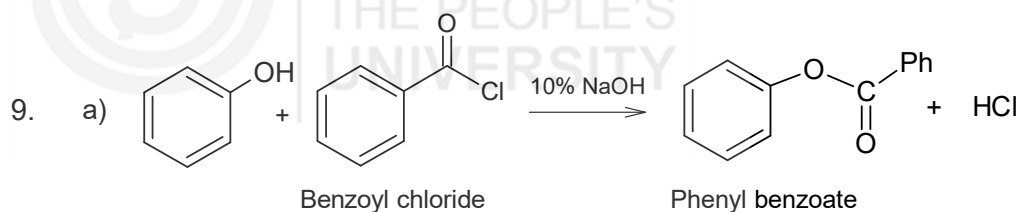


6. Similar to nitro group, aldehyde group contributes in delocalisation of negative charge of phenoxide ion.



7. Base is used as a catalyst to increase nucleophilicity by converting the nucleophile to an anion nucleophile. In case of phenols, the phenoxide ion is better nucleophile than unionised phenol.

8. 2-Hydroxybenzaldehyde

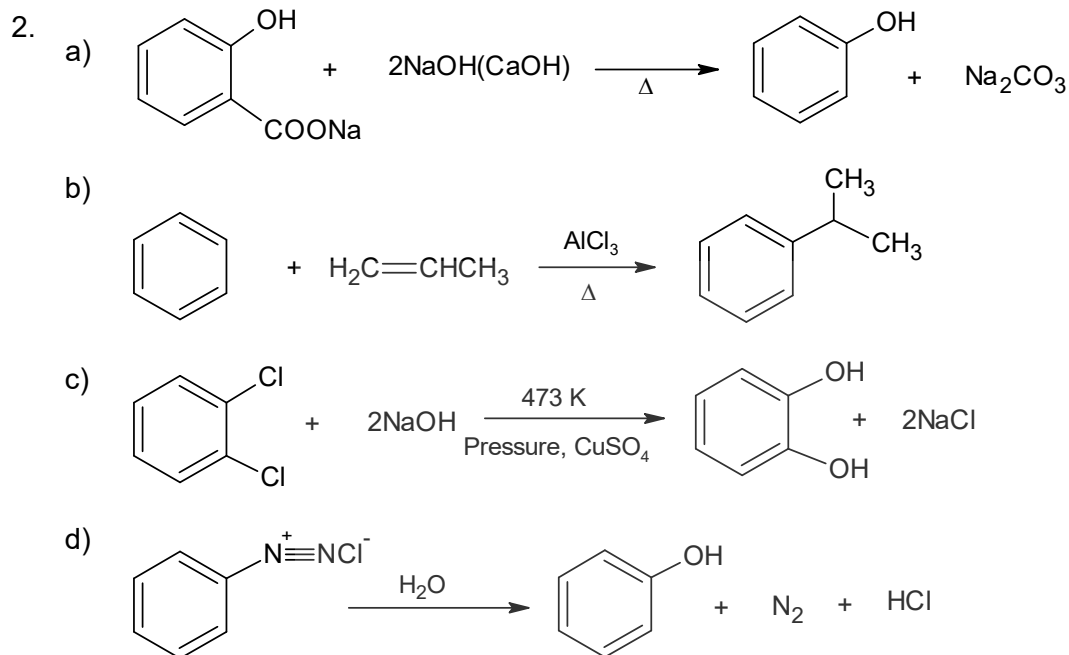


- c) See sub-section 16.5.4.

- d) See sub-section 16.5.4.

Terminal Questions

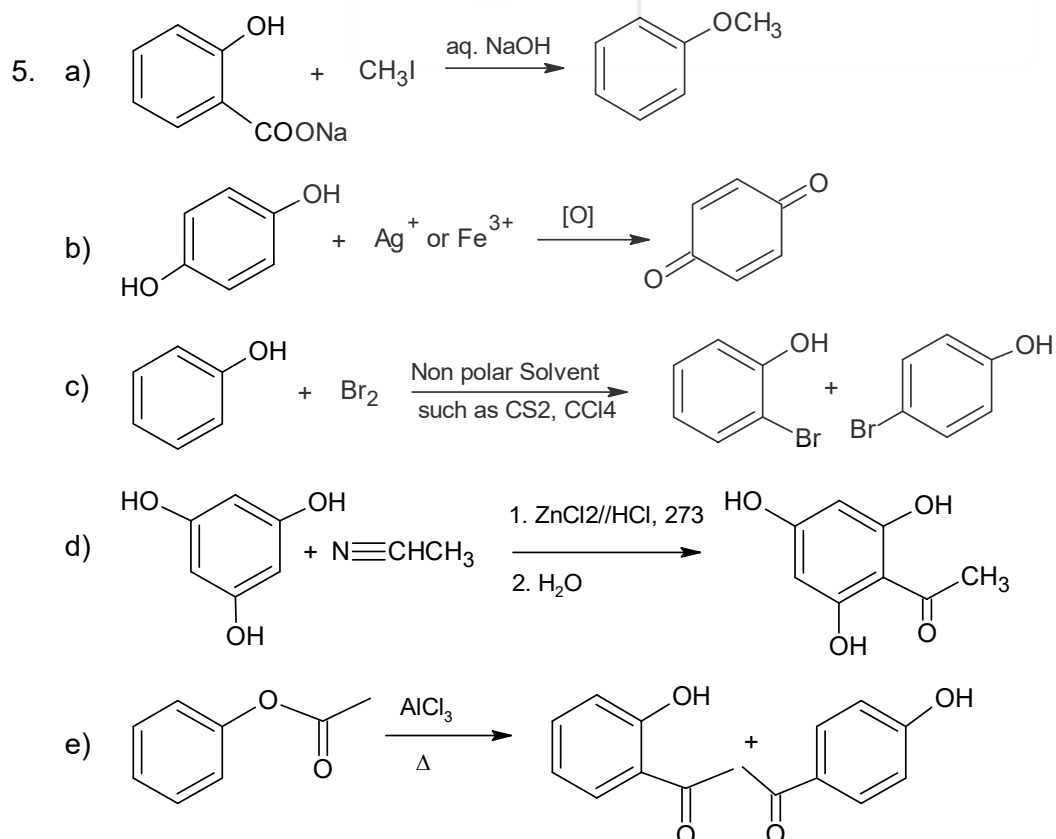
- a) 1,2,4-Benzenetriol; c) 2-Ethyl-4-nitrophenol;
 c) 3-Methyl-4-hydroxybenzaldehyde; d) 3-Chloro-4-fluorophenol.

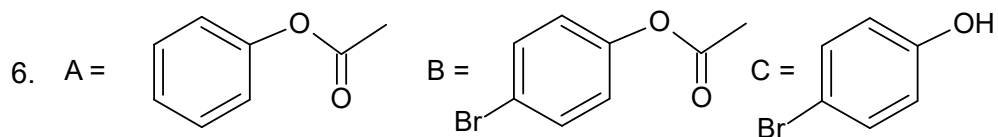


3. a) Phenol; b) 2,4-Dinitrophenol; c) p-Nitrophenol; d) 4-Hydroxybenzaldehyde

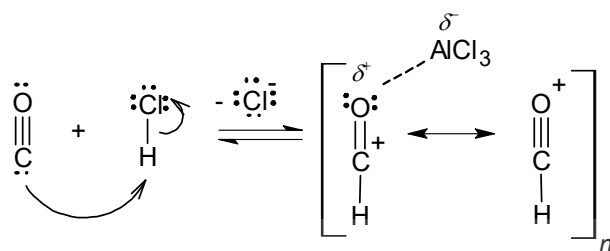
Explanation: Electron withdrawing group substituents increases the acidity of phenol, if such groups are at ortho and para to hydroxyl group this effect is more pronounced.

4. See page 169, Kolbe reaction.

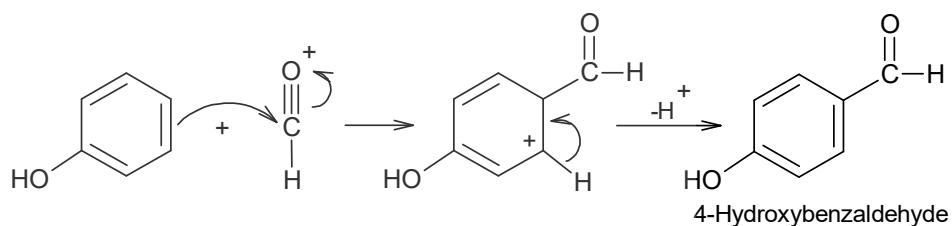




7. **Step 1:** Formation of formyl cation



Step 2: Electrophilic substitution of formyl cation



8. a) FeCl_3 solution test; b) Libermann's nitroso reaction

